

activity. On the other hand, among many kinds of zeolite, pentacyl-type zeolite, mordenite-type zeolite, β -type zeolite, and faujasite-type zeolite are widely used.

Page 2, first full paragraph:

β -type zeolite and faujasite-type zeolite have the pore apertures with the largest size of these zeolitezeolites. However, ~~not only~~ they have channels with large-size aperture ~~but and also~~ ~~they~~ have very large spaces formed by intersecting channels. Therefore, their drawback is that some undesired molecules (high-boiling-point compounds) are formed in the ~~intersection~~intersections of the channels with large space, and the undesired molecules thus formed therein ~~will finally clog~~clogs the pores to cause activity depression.

Paragraph bridging pages 2 and 3:

Being different from these catalysts, mordenite-type zeolite has no intersection of large-pore channels, and few undesired large-size molecules can be formed therein. But the aperture size of the pores therein is not so large ~~that and~~ it is not so effective for converting large-size molecules. Accordingly, the subject matterobject of the present invention is to solve the prior art problems, precisely to provide a highly-active, selective and long-life method for converting aromatic compounds having a large molecular size, concretely, for converting at least one aromatic compound selected from (a) aromatic compounds having at least three substituents, (b) aromatic compounds having two substituents of which at least one is a halogen or has at least 2 carbon atoms, and (c) naphthalene or anthracene derivatives having substituent(s).

Page 3, first full paragraph:

To attain the subject matter as above, the method for converting aromatic compounds of the invention principally comprises contacting at least one aromatic compound with a zeolite-containing catalyst, wherein the zeolite is characterized in that;

- (1) the minimum value of the pore aperture diameter of the major channels therein

is larger than 0.65 nanometers (hereinafter referred to as nm), or the maximum value thereof is larger than 0.70 nm, and

(2) the major channels do not intersect any others with larger apertures than an oxygen 10-membered ring;

and the aromatic compounds are at least one compound selected from the group consisting of:

(a) aromatic compounds having at least three substituents,

(b) aromatic compounds having two substituents of which at least one is a halogen or has at least 2 carbon atoms, and

(c) naphthalene or anthracene derivatives having substituent(s).

Page 4, second full paragraph:

The invention is described in detail hereinunder. Zeolite referred to herein is a crystalline microporous material which has the channels with uniform and molecular-level size pores, including crystalline aluminosilicate, crystalline metallosilicate, crystalline metalloaluminosilicate, crystalline aluminophosphate, crystalline metalloaluminophosphate, and crystalline silicoaluminophosphate. MetallosilicateThe metallosilicate and metalloaluminosilicate referred to herein are aluminosilicate derivatives in which aluminium is partly or entirely substituted with any other metals except aluminium, such as gallium, iron, titanium, boron, cobalt, chromium, etc. Similarly, metalloaluminophosphate indicates aluminophosphate derivatives in which aluminum or phosphorous is partly substituted with any other metals except it itself.

Paragraph bridging pages 4 and 5:

Zeolite for use in the invention is not specifically defined for its composition, for which various compositions such as those mentioned above are adopted. However, its structure is indispensably defined as follows:

(1) the minimum value of the pore aperture diameter of the major channels therein is larger than 0.65 nm, or the maximum value thereof is larger than 0.70 nm, and

(2) the major channels do not intersect any others with larger apertures than an oxygen 10-membered ring.

Page 5, first full paragraph:

In other words, the zeolite for use in the invention must satisfy the two requirements (1) and (2).

Paragraph bridging pages 5 and 6:

The major channels of the zeolite referred to herein are meant to indicate the channels having the largest pore apertures in one zeolite structure. The pore size in zeolite, in general, is represented by an expression of reference to an oxygen n-membered ring in which n indicates the number of oxygen atoms that constitute the pore aperture. For satisfying the requirement (1), the aperture size of the pores or channels must be at least equal to or larger than that of an oxygen 12-membered ring. Zeolite having channels of which the pore aperture size is larger than that of an oxygen 12-membered ring satisfies the requirement (1), but some others having the same will do not. For example, mordenite-type zeolite, though having oxygen 12-membered ring pores(channels), does not satisfy the requirement (1), since the minimum value of the pore opening diameter of the pores therein is 0.65 nm and the maximum value thereof is 0.70 nm. On the other hand, SSZ-31 of which the structure has been recently clarified (R.F. Lobo et al.; J. Am. Chem. Soc., Vol. 119, pp. 3732-3744, 1997) satisfies the requirement (1), since the maximum value of the pore opening diameter of the pores therein is 0.86 nm and the minimum value thereof is 0.57 nm. Zeolite having oxygen 12-membered ring pores and satisfying the requirement (1) in point of regard to the pore aperture diameter, and zeolite having pores larger than 12-membered ring pores in point of regard to the pore aperture diameter, for example, zeolite having 14-membered ring pores

are within the scope of zeolitezeolites for use in the invention.

Paragraph bridging pages 6 and 7:

Any one can know the sizesizes of pore apertures in zeolite of which the structure is known. Various types of zeolitezeolites of which the structure has been clarified, and the atomic configuration in such known different types of zeolitezeolites are described in Atlas of Zeolite Structure Types (W.M. Meier, D.H. Olson, Ch. Baerlocher, Zeolites, 17(1/2), 1996; Reference 1). In the section of Channels in Reference 1, they show the crystallographic free diameter. The free diameter values are based on any oxygen radius of 0.135 nm. In this shape, both the maximum value and the minimum value are shown for noncircular aperture. In this reference, the pore aperture is stereoscopically drawn as Fig. 1, and both its maximum value and the minimum value are given therein. The maximum value and the minimum value of the pore aperture referred to in the invention is just the values shown in the reference. For all types of zeolitezeolites clarified in Reference 1, their data of aperture size given in Reference 1 are referred to herein, irrespective of their composition, for judging their applicability to the invention (in fact, however, the pore size will vary, depending on the composition and the ambient temperature). For the others not shown in Reference 1 but disclosed in any other references such as journals and the like, their applicability to the invention will be judged in point of the pore aperture diameter from their structure disclosed in such other references.

Page 7, first full paragraph:

For the types of zeolite not clarified in Reference 1 in point of reference to their pore aperture diameter, the maximum value and the minimum value of the pore aperture therein shall be determined in a simplified method such as that mentioned below. Based on the atomic configuration and the space group of zeolitezeolites shown in references, a crystal model is constructed. For this, the atomic configuration and the space group are preferably

subject to a Rietveld refinement. The oxygen atoms constituting the pore aperture are combined with each other via a diagonal line drawn therebetween, and the maximum interatomic distance and the minimum interatomic distance are obtained (for this, the size of the oxygen atom itself is neglected, and the interatomic distance is obtained from the positional difference between the connected two oxygen atoms). From the maximum or minimum interatomic distance thus obtained, 0.27 nm (the diameter of one oxygen atom) is subtracted to give the maximum or minimum value of the pore opening size.

Paragraph bridging pages 7 and 8:

Zeolite having a larger pore aperture is more preferred for use in the invention, as having a higher conversion activity and ensuring a higher reaction yield. Therefore, it is desirable that both the minimum value and the maximum value of the pore opening diameter of the pores in zeolite for use herein are larger than 0.70 nm. For the pore entrance of the major pores in zeolite for use herein, larger pores than oxygen 12-membered ring pores are preferred to oxygen 12-membered ring pores. Though it is not clear, the reason will may be because molecules could diffuse more rapidly in larger pores in the zeolite. If molecules diffuse slowly in pores in zeolite, their reaction will be retarded, or that is, the reaction activity in the pore of such zeolite is poor. In addition, if molecules diffuse slowly in pores in zeolite, the time for which they are contacted with zeolite shall be prolonged, thereby often inducing side reactionreactions such as decomposition, and the reaction yield is lowered. Accordingly, enlarging the pore diameter in zeolite to promote the diffusion of molecules through the pores therein increases the conversion activity and the reaction yield. The uppermost limit of the pore diameter is not specifically defined, for which, however, it is desirable that the maximum value of the pore entrance diameter is at most 1.1 nm, more preferably at most 0.9 nm. Though it is not clear, the reason will may be because too large pores, if any in the zeolite, will provide a site for large molecules to be formed therein, and

high-boiling-point ~~substances~~substances thus formed therein will clog the pores to shorten the catalyst life of the zeolite.

Page 9, first paragraph:

Zeolite for use in the invention must satisfy not only the requirement (1) indicating that the minimum value of the pore aperture diameter of the major channels therein is larger than 0.65 nm, or the maximum value thereof is larger than 0.70 nm, but also the requirement (2) indicating that the major channels do not intersect with any others withthat have larger apertures than oxygen 10-membered ring pores.

Paragraph bridging pages 9 and 10:

For its pore structure, ~~zeolite has~~zeolites have one-dimensional pore systems or poly-dimensional pore systems. Preferably, zeolite for use in the invention has essentially one-dimensional pores. The pore structure of the one-dimensional pore system is generally such that the major channels do not intersect with any other channels having pore ~~sizes~~sizes not smaller than oxygen 7-membered pores. Being different from it, the pore structure of poly-dimensional pores is such that some major channels intersect some other channels with not smaller apertures that are not smaller than oxygen 7-membered ring pores. The invention is directed to conversion of aromatic compounds having a large molecular size, as will be described hereinunder, in which, therefore, ~~zeolite~~zeolites having small pores that are not larger than oxygen 10-membered ring pores is are substantially useless, since the pores therein are too small to be effective for to perform the intended conversion. Accordingly, in the invention, it is recognized that the pore ~~structure~~structures of ~~zeolite~~zeolites in which the major channels intersect the other pores not larger than oxygen 10-membered ring pores is are substantially one-dimensional, and ~~zeolite~~zeolites of the type having such a one-dimensional pore structure is are within the scope of ~~zeolite~~zeolites for use in the invention. On the other hand, zeolite in which large channels intersect with each other, for example,

β -type zeolite in which oxygen 12-membered ring pores intersect with each other shall have an extremely large space around the intersecting points, and undesirable reaction to give reactions yielding high-molecular-weight substances will be inevitable in such a large space in this type of zeolite. The high-molecular-weight substances thus formed in the large space will clog the pores, whereby the activity of the zeolite will be lowered. This is the reason why one-dimensional pore-structured ~~zeolite is zeolites are~~ preferred for use in the invention. Zeolite in which some major channels intersect some other channels with having not larger apertures than oxygen 10-membered ring will have substantially no other open pores except the major channels, and this type of zeolite is adopted in accordance with the invention without problem. Preferably, however, in zeolite for use in the invention, the channels that may intersect the major channels do not have larger pores than an oxygen 10-membered ring.

Paragraph bridging pages 10 and 11:

The structure of zeolite for use in the invention is not specifically defined provided that it satisfies the requirements defined herein. With reference to the structural code of three letters indicated in Atlas of Zeolite Structure Types (W.M. Meier, D.H. Olson, Ch. Baerlocher, Zeolites, 17(1/2), 1996), concretely, the structure of zeolite for use in the invention includes VFI, AET, AFI, AFR, AFS, ATS, BOG, BPH, DFO, GME, LTL, MAZ, MEI, OFF. In addition, it further includes CFI having large pores of which the pore entrance diameter is larger than that of oxygen 12-membered ring pores (M. Yoshikawa et al., Journal of Physical Chemistry, B, Vol. 102, pp. 7139-7147), and UTD-1 (R.F. Lobo et al., Journal of American Chemical Society, Vol. 119, pp. 8474-8484, 1997). Further, SSZ-31 mentioned above is also within the scope of zeolite for use in the invention. Of those, preferred for use herein are AFI, GME, LTL, MAZ, MEI, OFF, CFI, UTD-1, and SSZ-31; more preferred are CFI and UTD-1; even more preferred is CIT-5 zeolite. The structure type

code of which this zeolite is CFI.

Page 11, last paragraph:

Those types of zeolitezeolites may be natural ones or synthetic ones. Preferred is synthetic zeolite, as its composition can be controlled in any desired manner. Any known method can be adopted for producing it. For zeolite of which the structure is not clarified as yet, it will be impossible to identify the pore aperture diameter. ~~If such a case of~~ If such ~~a~~ case of large crystals of zeolite are prepared, the structure of the zeolite ~~shall~~may be determined according to an M. Yoshikawa et al's method (Journal of Physical Chemistry, B, Vol. 102, pp. 7139-7147, 1998) or to a C.C. Freyhardt et al's method (Journal of American Chemical Society, Vol. 118, pp. 7299-7310, 1996).

Paragraph on page 12:

Specific examples of zeolite structurestructures for use in the invention are mentioned hereinabove, and the composition of zeolite can be selected with reference to the intended reaction. For acid catalyst reaction, preferably used is any of crystalline aluminosilicate, trivalent metal-containing crystalline metallosilicate, and crystalline silicoaluminophosphate; more preferred are crystalline aluminosilicate and crystalline gallosilicate; and even more preferred is crystalline aluminosilicate. In crystalline aluminosilicate and metallosilicate for use in the invention, the ratio (by mol) of Si/(trivalent metal) is not specifically defined, but preferably falls between 5 and 500, more preferably between 5 and 200, even more preferably between 7 and 100. Zeolite having a smaller ratio of Si/(trivalent metal) will have a larger number of active pointsites, and is therefore preferred for use in the invention. On the other hand, zeolite having a larger ratio of Si/(trivalent metal) will be more hydrophobic, and is therefore preferred for conversion of organic compounds, since it can more easily absorb the reaction substrate. Zeolite having a well-balanced ratio of Si/(trivalent metal) in consideration of these facts ~~will~~may be suitably selected for use in the invention. For

oxidation with hydrogen peroxide, preferred is crystalline titanosilicate. For hydroxylation with nitrogen suboxide, preferred is crystalline ferrosilicate.

Page 13, first paragraph:

In case ~~where~~the zeolite for use in the invention has ion-exchanging sites, the sites may be ion-exchanged with any other different ions. In case ~~where~~the zeolite is used herein as an acid catalyst, in general, it is previously subjected to a few times of ion exchange treatment with an aqueous solution of an ammonium salt and then calcined to be an acid-type zeolite catalyst.

Page 13, last paragraph:

For preferable use in the invention, the zeolite is formed. Zeolite alone may be formed, or may be granulated along with a binder such as alumina, clay, etc. For granulating it, for example, the zeolite is kneaded with a binder such as alumina or the like, then extruded out through an extruder, and rounded into granules by the use of an equipment like Marumerizer (a type of granulator, pelletizer or the like).

Page 14, first paragraph:

From the zeolite-containing catalyst, in general, crystal water existing therein and organic substances used in producing it and still remaining therein are removed before use. In general, it may be heated at 200 to 600°C, whereby crystal water and the organic substances ~~could~~can be almost completely removed from zeolite.

Page 14, second paragraph:

The catalyst may contain metal. For example, it is desirable to prolong the catalyst life that the acid catalyst contains a noble metal, and the reaction is carried out in the presence of hydrogen. Though not clear, the reason ~~will~~may be because the catalyst could more readily receive protons and it could be prevented from coking. The noble metal that may be in the catalyst is not specifically defined, but rhenium is the best. The reason ~~will~~

beis because the catalyst containing rehenium will hardly undergo hydrogenolysis.

Page 15, first paragraph:

The aromatic compounds in the invention are limited to those having a relatively large molecular size. For converting compounds having a small molecular size, such as xylene, toluene and others, conventional pentacyl-type zeolite (MFI) and mordenite-type zeolite (MOR) will give enough reaction property but they ~~are~~ do not give enough reaction property for converting aromatic compounds having a large molecular size. The method of the invention is directed to the efficient conversion of such aromatic compounds having a relatively large molecular size. Aromatic compounds having a relatively large molecular size in the invention are at least one selected from:

- (a) aromatic compounds having at least three substituents,
- (b) aromatic compounds having two substituents of which at least one is a halogen or has at least 2 carbon atoms, and
- (c) naphthalene or anthracene derivatives having substituent(s).

Page 20, first full paragraph:

Ludox HS-30 (from DuPont) was used as a silica source; aluminium nitrate 9-hydrate (from Nakarai Tesq) was used as an aluminium source; and anhydrous lithium hydroxide (from Kishida Chemical) was used as a lithium source. From these, prepared was a mixture having a composition formula, $\text{SiO}_2:0.1\text{LiOH}:0.2\text{MeSPA OH}:0.01\text{Al}(\text{NO}_3)_3:40\text{H}_2\text{O}$ (by mol).

Page 20, second full paragraph:

The mixture was stirred for 2 hours, and then heated in a Teflon lined autoclave at 175°C for 9 days. The resulting zeolite was taken out through filtration, washed with water, dried at 100°C and analyzed through X-ray diffractiometry, by which it was identified as CIT-5. According to the reference (M. Yoshikawa et al's Journal of Physical Chemistry,

B, Vol. 102, pp. 7139-7147, 1998), the zeolite CIT-5 contains oxygen 14-membered ring pores, and the pore aperture is nearly circular and has a diameter of about 0.73 nm. In this, the major channels do not intersect any other pores.

Page 22, first full paragraph:

The relative ratio of 2,4-DCT conversion per one active site of the catalyst used was as follows: The number of the active pointsites in each catalyst was determined from the amount of aluminium in zeolite. The degree of conversion was determined from the weight loss of 2,4-DCT before and after the reaction.

Version with Markings to Show Changes to the Claims

Kindly amend the claims as follows:

1. (Amended) A method for ~~convertingisomerizing~~ aromatic compounds, which comprises contacting at least one aromatic compound with a zeolite-containing catalyst, and in which the zeolite is characterized in that;:

(1) the minimum value of the pore aperture diameter of the major channels therein is larger than 0.65 nanometers, or the maximum value thereof is larger than 0.70 nanometers, and

(2) the major channels do not intersect any others with larger apertures than oxygen 10-membered ring;

and the aromatic compounds are at least one selected from; the group consisting of:

(a) aromatic compounds having at least three substituents,

(b) aromatic compounds having two substituents of which at least one is a halogen or has at least 2 carbon atoms, and

(c) naphthalene or anthracene derivatives having substituent(s).

2. (Amended) The method for ~~convertingisomerizing~~ aromatic compounds as claimed in claim 1, wherein the minimum value of the pore aperture diameter of the major channels in the zeolite is not smaller than 0.7 nanometers.

3. (Amended) The method for ~~convertingisomerizing~~ aromatic compounds as claimed in claim 1 or 2, wherein the pore aperture size of the major channels in the zeolite is larger than oxygen 12-membered ring.

4. (Amended) The method for convertingisomerizing aromatic compounds as claimed in ~~any one of claims~~claim 1 to 3 or 2, wherein the catalyst is contacted with a substituted aromatic compound in which at least one substituent is a halogen.

5. (Amended) The method for convertingisomerizing aromatic compounds as claimed in ~~any one of claims~~claim 1 to 4 or 2, wherein the catalyst is contacted with an aromatic compound having at least three substituents.

Kindly add the following new claims:

6. (New) The method according to Claim 1, wherein said zeolite is one selected from the group consisting of SSZ-31, VFI, AET, AFI, AFR, AFS, ATS, BOG, BPH, DFO, GME, LTL, MAZ, MEI, OFF, CFI having large pores of which the pore entrance diameter is larger than an oxygen 12-membered ring pore, and UTD-1.

7. (New) The method according to Claim 1, wherein the maximum value of a pore entrance diameter is at most 1.1 nm.

8. (New) The method according to Claim 1, wherein said zeolite has a one-dimensional pore system.

9. (New) The method according to Claim 1, wherein said zeolite is synthetic.

10. (New) The method according to Claim 1, wherein said zeolite has a crystal size of at most 1 μm .

11. (New) The method according to Claim 1, wherein said zeolite is formed.

12. (New) The method according to Claim 1, wherein said catalyst contains metal.

Version Showing Changes Made to the Abstract

According to a method for converting isomerizing aromatic compounds, which comprises contacting wherein at least one aromatic compound is contacted with a zeolite-containing catalyst, and in which the zeolite is characterized in that;:

(1) the minimum value of the pore aperture diameter of the major channels therein is larger than 0.65 nanometers, or the maximum value thereof is larger than 0.70 nanometers, and

(2) the major channels do not intersect any others with larger apertures than oxygen 10-membered ring;

and the aromatic compounds are at least one selected from;

(a) aromatic compounds having at least three substituents,

(b) aromatic compounds having two substituents of which at least one is a halogen or has at least 2 carbon atoms, and

(c) naphthalene or anthracene derivatives having substituent(s),

wherein aromatic compounds having a relatively large molecular size can be efficiently converted isomerized.

Remarks

We note with appreciation the acknowledgment of the claim for foreign priority under 35 U.S.C. §119. The Specification and Abstract have been amended to correct minor typographical errors and to improve readability. Claims 4 and 5 have been amended to proper multiple dependent form. Claims 6-12 have been added. Thus, Claims 1-12 are present in the case. No new matter has been added.

Turning to the merits of the application, we respectfully submit that the present invention as defined by the solicited claims is patentably distinct over the cited prior art references for the reasons detailed hereinafter. It should be noted that U.S. Patent 6,043,179 to Davis, et al. ("Davis") shares a common inventor with the present application. As such, it is significant that the Applicant is highly familiar with the Davis disclosures and considers the present invention to be patentably distinct over that reference.

The invention is directed to a method for *isomerizing* an aromatic compound of large molecular size using a zeolite-containing catalyst, as supported in the Specification at page 17. The aromatic compound isomerized according to the method of amended Claim 1 may be one selected from an aromatic compound having at least three substituents; an aromatic compound having two substituents, at least one of which is halogen or has at least two carbon atoms; or naphthalene or anthracene derivatives having substituents, as supported at page 15, line 1 to page 17, line 1 of the Specification. As explained in the Specification at page 1, line 19 to page 2, line 2 and elsewhere, isomerization of large size molecules such as these using zeolite having small pores or intersecting pore channels is problematic because the molecules are unable to rapidly diffuse to the pores to achieve efficient isomerization. Thus the characteristics of the zeolite catalysts that are effective for such isomerization reactions are defined in Claim 1.

In sharp contrast, the prior art references fail to disclose isomerization of the aromatic compounds as set forth in Claim 1. Specifically, Davis discloses at Column 15, line 20 to Column 16, line 26 only alkylation and transalkylation of an aromatic hydrocarbon. Alkylation and transalkylation involve the transfer of an alkyl group from one molecule (the

alkylating or transalkylating agent) to the reactant molecule being converted, as distinguished from the claimed isomerization reaction. Likewise, U.S. patent No. 5,215,648 to Zones et al. ("Zones") teaches at Column 16, lines 4-58 only alkylation and transalkylation of an aromatic hydrocarbon. Furthermore, WO 97/46486 discloses only alkylation and transalkylation of aromatic hydrocarbon feedstocks (page 23). We respectfully submit that none of the cited prior art references teaches or even suggests isomerization of the aromatic compounds. As such, the cited prior art references do not anticipate Claims 1-12 as amended.

Furthermore, it would be in error to suggest that it would have been obvious to one having ordinary skill in the art at the time of the invention to modify the prior art methods by substituting in the conversion reaction a halogenated aromatic compound for the disclosed aromatic compounds. As explained at page 16, line 7 to page 17, line 1 of the Specification, an aromatic compound having two substituents of which one is a halogen refers to a compound having at least one bulky substituent. Unlike the aromatic compounds converted by the prior art methods, the halogenated aromatic compounds converted by the present method are subject to the unique risk of dehalogenation. Thus, the method of the present invention is especially effective for aromatic compounds having halogen substituents since the bulky halogenated aromatic compounds are able to diffuse easily through the specified zeolite catalysts without risk of being dehalogenated. As a result of these chemical and physical dissimilarities between the bulky halogenated aromatic compounds of the solicited method and the non-halogenated aromatic compounds of the prior art, we respectfully submit that the present invention was not obvious to one of ordinary skill in the art based on the cited prior art disclosures.

Moreover, even assuming *arguendo* that it would have been obvious to modify the prior art methods by employing a halogenated aromatic compound, the resulting method would not amount to this invention as defined by the amended claims. Specifically, not one of the cited prior art references teaches or even suggests isomerization of the aromatic

compounds of Claim 1. We therefore respectfully submit that Claim 4 is patentably distinct over the cited prior art.

Applicants have discovered a new and useful method for isomerizing aromatic compounds using a zeolite-containing catalyst. In light of the foregoing, we respectfully submit that Claims 1-12 are in proper form for allowance. We accordingly respectfully request early notification to that effect.

Respectfully submitted,



T. Daniel Christenbury
Reg. No. 31,750
Attorney for Applicants

TDC/FG:dh
(215) 563-1810